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To: Dr. D. Mills
Director of Research

LASER RAMAN SPECTROSCOPY AS A PROBE OF SURFACE STRUCTURES

L. Mannik

Laser Raman spectroscopy is an optical scattering technique which is useful in identifying the molecular structure of solid surfaces. The present study has focused on two specific materials, the recently discovered ceramic high temperature superconductors and the surface oxide on the Zr-2.5% Nb alloy used for CANDU pressure tubes. In each case, Raman spectra obtained with an argon ion laser and a single grating monochromator yielded information on the phases present in the samples. This diagnostic technique has the potential for being extended in the near term to *in situ* pressure tube corrosion studies in the laboratory and in the longer term to on-line measurements in a variety of applications including the monitoring of corrosion in heat exchangers and of hydride formation in pressure tubes.

INTRODUCTION

There is an ever-increasing need in Ontario Hydro for methods of analyzing the structure of materials and how this structure is altered during service. An example is the current interest in the hydriding and oxidation of pressure tubes in nuclear reactors. An optical technique, laser Raman spectroscopy, may have a contribution to make in this area since it is capable of providing quick, on-line information on the molecular structure of solid surfaces and can be designed to operate in adverse environments. This report outlines the basic concept of this diagnostic tool and presents the results of preliminary laboratory measurements.

When monochromatic light is incident on a gas, liquid or solid, scattered light is observed not only at the incident frequency (elastic or Rayleigh scattering) but also at slightly shifted frequencies. These frequency shifts correspond to the vibrational frequencies of the molecules in the scattering medium and the process is known as Raman scattering, named after the discoverer of the phenomenon. The emission lines characterized by a shift to lower frequencies are called the Stokes components and these are more intense than the anti-Stokes lines which occur at frequencies greater than the excitation frequency.

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Since the Raman effect is based on the scattering of light due to an induced dipole moment in the molecule, it provides information on molecular vibrations that is complementary to infrared absorption which is associated with a permanent dipole moment. Also, since the effect can be observed with any excitation frequency, experiments can be designed with ultraviolet or visible light sources to enhance the scattered light output. After the initial discovery involving molecular vibrations, Raman spectroscopy was extended to include the study of transitions associated with molecular rotational frequencies, electronic transition frequencies and phonon modes (lattice vibrations) in solids.

The main drawback of Raman spectroscopy is the extremely low efficiency of the light scattering process. The intensity of the inelastically scattered light is typically 10^{-7} to 10^{-15} of the intensity of the incident light. This is one reason that the application of high intensity lasers to Raman spectroscopy revolutionized the technique in the 1960's. Two other advantages of the laser as a light source are its narrow line-width, which enables low frequency shifts to be detected, and its low beam divergence, which permits tight focusing of the incident light. This allows spatially localized Raman spectroscopy to be performed, which is especially important for solid state applications. A recent development is the use of optical fibers for light delivery and collection, which enables the technique to be adapted to the monitoring of otherwise inaccessible areas.

Today Raman spectroscopy is applied to a wide variety of analytical problems associated with the determination of molecular structures including fingerprinting, structural analysis of polymers and concentration and temperature measurements in flames. The technique is also applicable to the study of solid surfaces, being capable of providing quick and unambiguous identification of compounds present in surface films as thin as 50A (5×10^{-3} μm)/1/. It is especially useful in detecting phase transformations because it is sensitive to changes in the crystal structure/2/. Raman spectroscopy has also been used to study the composition of oxidation and corrosion products on metal surfaces/3, 4/.

At the Research Division two applications of the Raman spectroscopy of solids have recently been explored. The first involves a study of the feasibility of using *in situ* Raman spectroscopy as a method of monitoring oxide growth in samples of Zr - 2.5% Nb pressure tube material. The second arose out of the discovery of high temperature superconducting materials and the need to characterize samples fabricated at Ontario Hydro. The results of preliminary investigations in these two areas are described below.

EXPERIMENTAL ARRANGEMENT

Figure 1 is a schematic diagram of the experimental arrangement for the laser Raman spectroscopy. The argon ion laser (Lexel Model 85) emits up to 250 mW of single-mode power at 514.5 nm; it is equipped with a line-narrowing etalon since it is normally used in holographic research. Removing this etalon would result in 1 W of multi-mode output, which is adequate for Raman spectroscopy. The laser energy is focused onto the sample after passing through a filter to

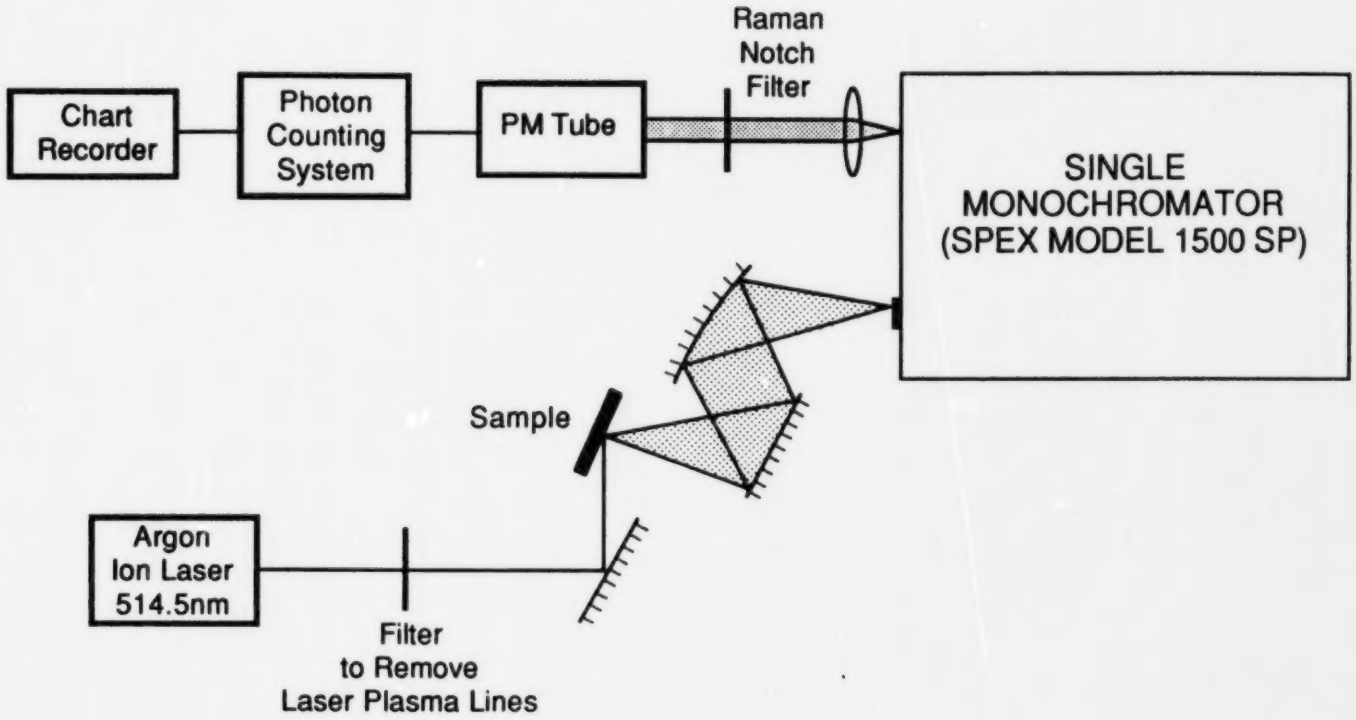

FIGURE 1

EXPERIMENTAL ARRANGEMENT FOR RAMAN SPECTROSCOPY

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remove the various plasma emission lines which are present in addition to the 514.5 nm line.

The light scattered from the sample is collected at 60° from the normal to the surface and is focused onto the entrance slit of the monochromator. The latter is a Spex Model 1500SP single grating instrument which is not normally considered suitable for Raman spectroscopy because of its poor stray light rejection compared to double grating monochromators. However, double monochromators are expensive (US $25K) and suffer from reduced throughput (10%, compared to 30% for single monochromators). Therefore we resorted to the use of a special "Raman notch" filter manufactured by Omega Optical to reject the 514.5 nm energy elastically scattered by the sample. This filter's transmission is less than 10^{-5} at the rejection wavelength. In the region of interest for Stokes Raman spectroscopy, the filter has a transmission of 20% for a 200 cm^{-1} frequency shift, rising to 60% for a 500 cm^{-1} shift. The monochromator slit width ranged from 400 to 800 μm. Signal detection was performed with a photomultiplier connected to conventional photon counting electronics supplied by Ortec.

EXPERIMENTAL RESULTS

a) Zirconium Oxide

Figure 2 shows the Raman spectrum measured for a sample of Zr - 2.5% Nb. This material was prepared by exposing a piece of pressure tube for 24 hours in 400°C steam at 150 psi. The thickness of the resulting oxide was 1 to 2 μm.

The two main bands at 480 and 635 cm^{-1} are consistent with published Raman spectra of zirconium oxide or zirconia/1/. In fact, the 480 cm^{-1} band is characteristic of the monoclinic phase of zirconia and the band at 635 cm^{-1} is associated with the tetragonal phase. These preliminary results suggest the possibility of using Raman spectroscopy to provide *in situ* data on oxide growth as part of a laboratory investigation of pressure tube corrosion.

Among the parameters that could be monitored in such an application are the spatial variation in the oxide phase which would show up as a changing pattern of Raman bands at different locations on the surface. With the 5.5 cm focal length lens used in these experiments the focused spot size is less than 100 μm. It may also be possible to gain a measure of the oxide thickness over a limited range from the strength of the Raman bands. Less probable, but also worth considering, is the detection of Raman bands due to impurities in the oxide. Plans are under way to design a Raman facility in conjunction with an autoclave being constructed by Metallurgical Research for pressure tube corrosion studies.

b) High Temperature Superconductors (HTSC)

Shortly after unsuccessful attempts to obtain a Raman spectrum of $YBa_2Cu_3O_7$ using samples prepared at Brock University and at OHRD, preprints of two papers dealing with this subject were received/5, 6/. These publications made

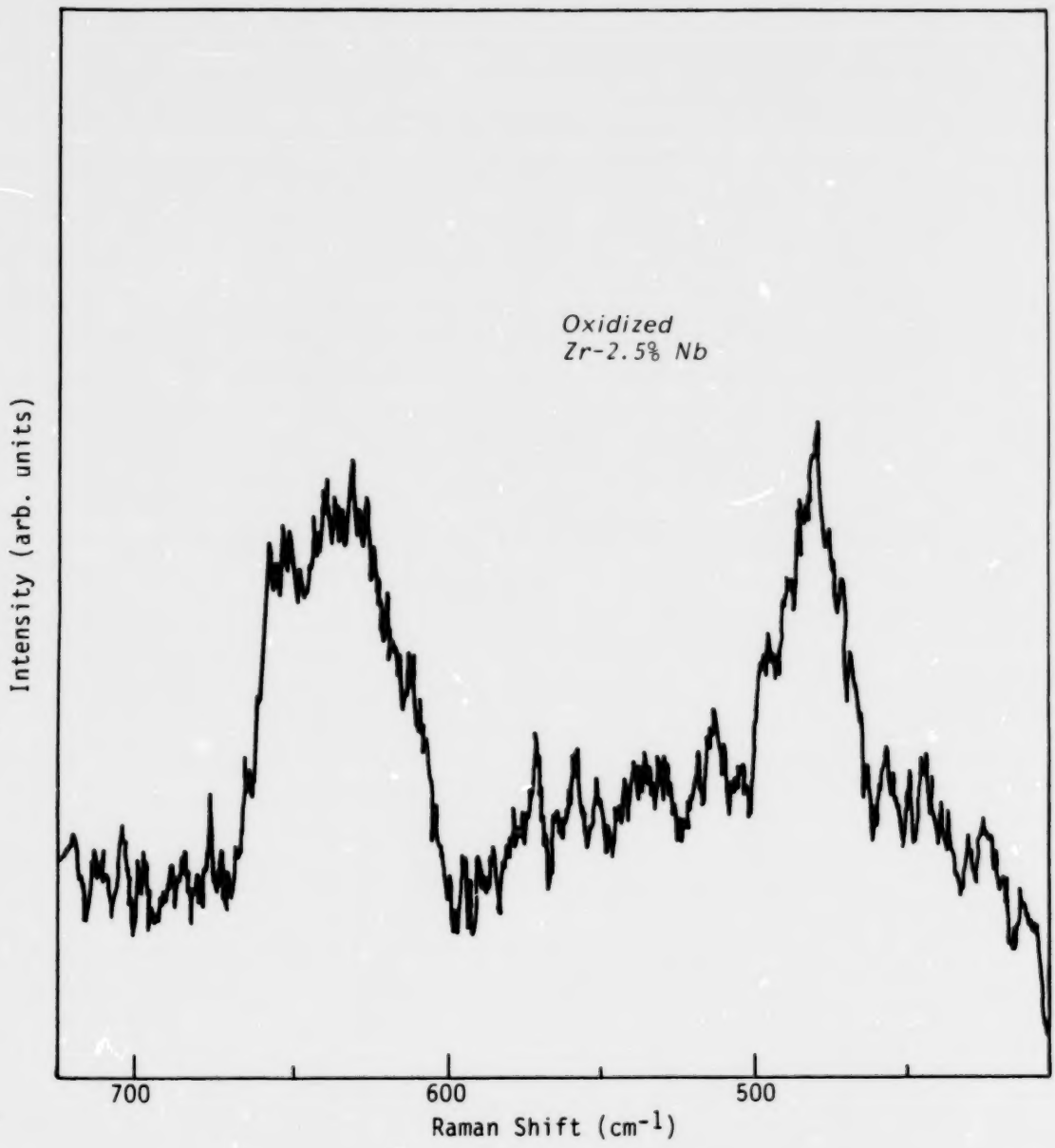

FIGURE 2

MEASURED RAMAN SPECTRUM OF
OXIDIZED PRESSURE TUBE MATERIAL

it clear that of the three versions of HTSC that were investigated ($XBa_2Cu_3O_7$, X= Y, Eu, Sm), $YBa_2Cu_3O_7$ yielded the weakest Raman spectrum, consisting of a weak band at 505 cm^{-1}. The strongest spectrum was obtained with Eu material but, since this was also the most expensive to fabricate, it was decided to investigate the Sm material. Samples of $SmBa_2Cu_3O_7$ were prepared at OHRD and the Raman spectrum shown in Figure 3 was observed. The frequencies of the observed Raman shifts are similar to those of the other investigators (Table 1). Note that there is apparently no effect of the different temperatures used in the three studies. This is consistent with the results of Ref. 6 in which no significant changes in the Raman spectra were observed over the range 7K to 300K.

TABLE 1. Frequencies (cm^{-1}) of Raman bands observed for HTSC.

Bell Labs. (Ref. 5)	Max Planck (Ref. 6)			This work
$EuBa_2Cu_3O_7$ (T = 77K)	$YBa_2Cu_3O_7$	$EuBa_2Cu_3O_7$ (T = 7K)	$SmBa_2Cu_3O_7$	$SmBa_2Cu_3O_7$ (T = 300K)
433	-	432	432	425
501	505	505	505	515
592	-	584	-	580
644	-	640	-	639

Reference 6 contains a preliminary analysis of the Raman-active vibrations of this class of superconductors. The conclusion is that the two lower frequency bands (432 and 505 cm^{-1}) arise from Cu-O stretching vibrations in the molecule. In Reference 6, the two higher frequency bands (584 and 640 cm^{-1}) were only observed for the EuHTSC which was also the only one of the three materials to show evidence of a second phase based on electron diffraction measurements. Therefore these bands were ascribed to defect-induced scattering arising from this second phase. Presumably the Bell Labs EuHTSC sample and our SmHTSC sample also contained such a second phase.

Following these measurements we made renewed attempts to detect the Raman spectrum of the Y samples, but without success. It is possible that the explanation lies in the degradation of the samples due to exposure to water vapor. Such degradation has been shown by electron microscopy and X-ray diffraction to lead to changes in the structure of the material/7,8/ and therefore the Raman spectrum could also be affected.

OTHER APPLICATIONS

The success in measuring the Raman spectrum of the surface oxide in Zr-2.5% Nb suggests the possibility of using the technique for the characterization of other types of oxides. A recent attempt in our laboratory to detect the ~20 Å thick oxide on a sample of Monel 400 heat exchanger material proved unsuccessful, but it should be possible to measure the Raman bands arising from thicker oxides in the 1 μm range. Such data could help to explain the fact that similar heat exchanger materials have exhibited widely differing resistance to corrosion/9/. There may be opportunities in the future to combine Raman scattering with optical fibers to develop a method of on-line heat exchanger corrosion monitoring.

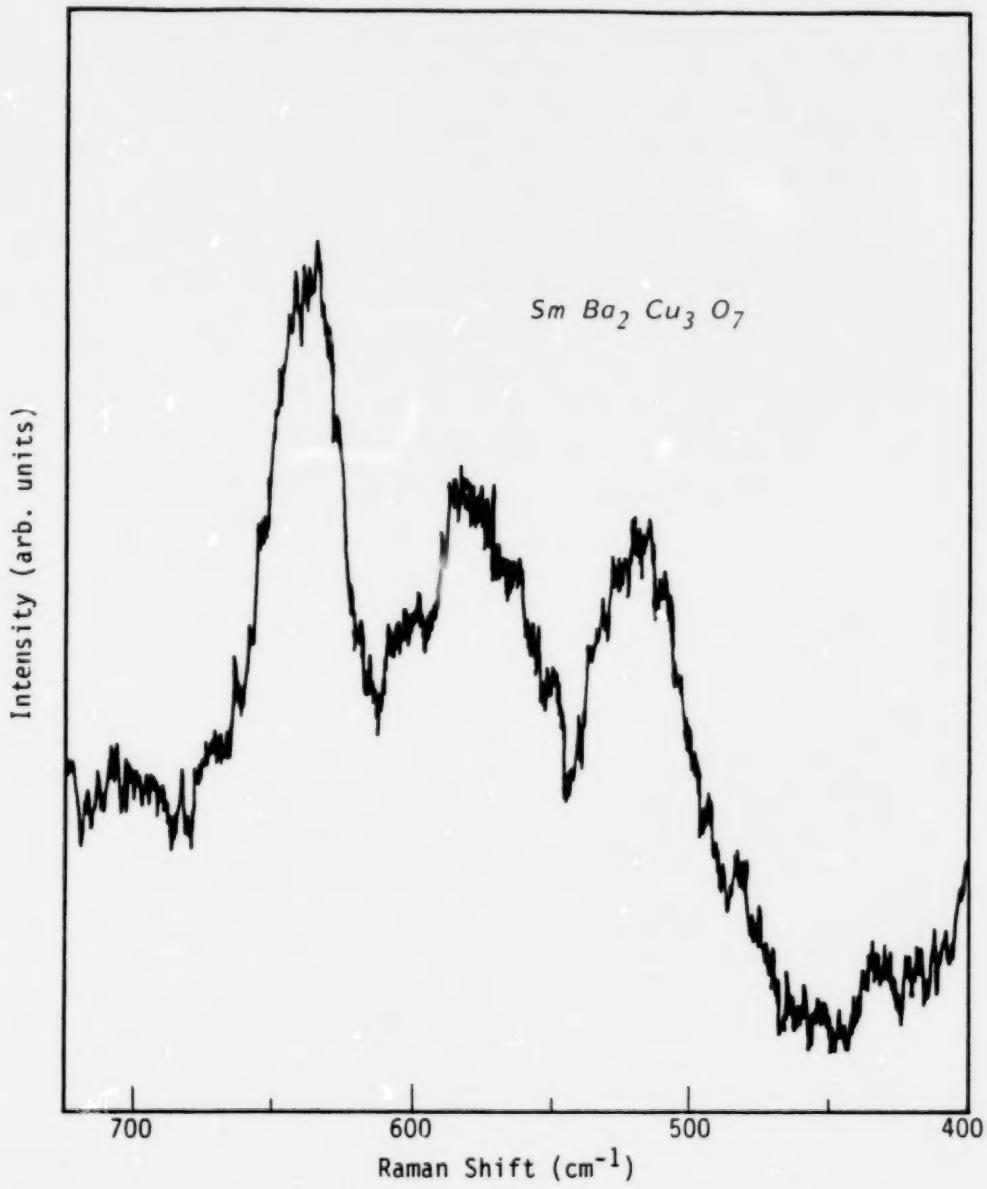

FIGURE 3
MEASURED RAMAN SPECTRUM OF $SmBa_2 Cu_3 O_7$
HIGH TEMPERATURE SUPERCONDUCTOR

In our nuclear reactors, there is a need for an on-line method of monitoring the build-up of zirconium deuteride in the pressure tubes. Laser Raman spectroscopy could potentially be used to characterize deuteride formation on the surface of pressure tubes. However the use of optical fibers for light delivery would be limited to low-field areas outside the biological shield because of the radiation resistance of currently available optical fibers (10^7 rads). In the high-field areas it may be possible to use a metal waveguide in the annulus to perform the light delivery function/10/.

SUMMARY AND CONCLUSIONS

1. The feasibility of measuring the Raman spectra of solids has been demonstrated, using an argon ion laser and a single-grating monochromator combined with a notch filter.

2. The Raman spectrum of oxidized Zr - 2.5% Nb can be used to provide information on the structure of the zirconium oxide and therefore may be applicable to *in situ* corrosion studies.

3. The Raman spectrum of high temperature superconductors of the type $XBa_2Cu_3O_7$ yields information on the phases present in the sample.

4. Laser Raman spectroscopy has the potential of being applied to other areas of interest including the monitoring of oxide growth in heat exchangers and of deuteride formation in pressure tubes.

Approved:

A.F. Baljet
Manager
Electrical Research Dept

Submitted:

L. Mannik
Engineering Physicist
Science Section

LM/mf/lct

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